Interaction of L-Threonine in aqueous THFA and in mixed aqueous solution at 298.15K

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Abstract:

Densities ρ and viscosities η of L-Threonine in water and in mixed aqueous solution of tetrahydrofurfurylalcohol at 298.15K. On the basis of these data ,the apparent molal volumes ϕ_v ,partial molal volumes at infinite dilution $\phi_v°$, the slop S_v ,transfer volume $\phi_v°$ (tr) , Gibbs free energy of activation for viscous flow of solution $\Delta G^*_{1,2}$ and the B-coefficient have been calculated using Jones-Dole equation . The obtained thermodynamic properties have been discussed in terms of intermolecular interactions.

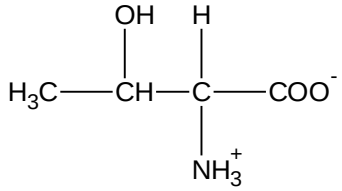
Key word: viscosity, density, L-Threonine, tetrahydrofurfurylalcohol.

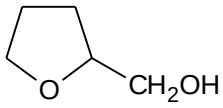
Introduction

In order to understand various fundamental processes like denaturation of proteins, folding / lunfolding processes, stability of proteins etc. in aqueous solution , knowledge of various solute-solvent and solute – solute interactions is very important. Due to complex structure of proteins , direct investigation of the solute /solvent effect on these biological macromolecules is very challenging, therefore, a useful approach is to study simple model compounds such as amino acid which are the monomer units of proteins molecules. The interpretation of behavior of amino-acids is quite helpful in understanding the water-protein interactions in solutions.

Moreover volumetric, viscometric studies of amino acids in water and solutions of organic solvents can provide valuable information for understanding protein unfolding [1-3] and the hydrophobic interactions of non-polar side chains [4]. The amino acids are high water solubilities suggests that they exist in an ionic form (zwitter ion). In physiological media such as blood , membrans , cellular fluids , etc. , where happens to be involved in an important manner , the zwitter ionic (dipolar) character of these compounds has an important bearing on their biological functions [5]. The interactions occurring between amino acids and other components are

reflected by their thermodynamic properties [6-10]. L-threonine (abbreviated as Thr.), classified as polar amino acid, is an essential α-amino acid . It was discovered as last of 20 common proteinogenic amino acids with two chiral centers. Threonine is used for single enantionmer (25,3R). The water and THF has proved to be most interesting solution due to hydrogen bond interactions of water with THFA [11-13]. The mixed aqueous solvent (with different percent w/w) can influence the solubility behaviour of amino acids . Conaequently thermodynamic properties , enthalipes , heat capacities , apparent molal volumes and viscosities of amino acids and peptide in mixed aqueous solvents is useful to obtain information about various types of interactions in these solutions [14-19].





Threonine(Thr.) M=119 g mol^{-1}

Tetrahydrofurfurylalcohol(THFA) M=102.13 g mol^{-1}

Experimental

Amino acid L-Theonine obtained from fluka company is Analar and used without any further treatment. THFA was purchased from Merck with purity higher than 99% and used without further purifications.

The viscosity η were determined using as uspended –level ubbelohde viscometer described by findly [20], in a bath controlled to Foolk for all measurements.

Densities ρ of all solution were measured using avibrating tube digital Anton parr densimeter (DMA 60/602) according to shukluetal. Procedure [21] in a thermostated bath controlled to ± 0.01K.

Result and Discussion:

The apparent molal volume (ϕ_v) is calculated using the following equation

$$\phi_v = \frac{1}{m}\left[\frac{10^3 + mM}{\rho} - \frac{10^3}{\rho_\circ}\right] \quad \text{.....(1)}$$

Where ρ and $\rho_\circ$ are the densities of solution and solvent respectively, M is molecular weight of solute and m is the molality of

solution , m is calculated using the following relation $m = 1/(\frac{\rho}{c} - M/10^3)$ where c is the molar concentration . Since the limiting apparent molal volume (ϕ_v) were obtained from the relation [22].

$$\phi_v = \phi_v^\circ + S_v m \text{.....(2)}$$

Where ϕ_v° is the partial molal volume at infinite dilution which gives information about solute hydrophobicity , hydration properties and is also a measure of solute-solvent interaction.

S_v is slop indicating solute-solute interactions which is also known as volumetric pair wise interaction coefficient [23]. From transition state theory the Gibbs free energy of activation for viscous flow of solution ΔG^*(J.mol^{-1}) at a given temperature and composition is given by the equation [24-25].

$$\Delta G^* = RT \ln(\frac{\bar{V}_{1,2}\eta}{hN_A}) \text{.....(3)}$$

Where R is the gas constant , T is the absolute temperature , h is planks constant, N_A is Avogadro's number and volume of mole solution, $\bar{V}_{1,2}$ obtained from the following relation

$$\bar{V}_{1,2} = (10^3 + mM_2)/\rho(\frac{10^3}{M_1} + m) \text{.....(4)}$$

Where M_1 and M_2 are the molecular weight for solvent and solute respectively.

The viscosity measurements have been analyzed in terms of Jones-Dole equation [26].

$$\eta_r = \frac{\eta}{\eta_\circ} = 1 + BC \text{.....(5)}$$

Where C is the molarity of solution , $\eta_\circ$ and η are the viscosities of solvent and solution respectively used to calculate viscosity B-coefficients using Jones –Dole equation . The value of B depends upon the size of solute and nature of solute –solvent interactions which is definite for solute –solvent system .

The values of apparent molal volume ϕ_v calculated using equations1. A linear dependence of ϕ_v on molality is observed for all the concentrations investigated , the limiting apparent molal volume is calculated by linear square fit of ϕ_v versus molality plot using equation 2. The value of limiting apparent molal volume has been found to be positive , showing the presence of strong solute-solvent interaction , ϕ_v° values

increases as the concentration increases indicating that the solute –solvent interaction increases on increasing the concentration of solute as well as solvent.

The values of ΔG* is calculated via equation 3, the values of ΔG* increasing with increasing THFA% in solution .

The viscosity of Threonine in water increases with increase in concentration of solute. The viscosity of water plus THFA in the absence of Threonine (stock solution) is slightly more than the viscosities when Threonine is add to it. However, the viscosity of threonine in the presence of water and THFA(solvent) at different molarities increase.

It evidences the existence of molecular interactions occurring in the system. In terms of Jones-Dole coefficients gives the value of transfer B-coefficient. The coefficient B represents measure of order or disorder introduced by co-solute in to water. The value of B-coefficients is positive which shows strong alignment of THFA with Threonine and thus higher B-coefficients at high concentrations of these organic solutes, thus the positive values of B-coefficients suggesting the solute-solvent interactions.

The standard partial molar volumes of transfer, $\phi_v^\circ\ (tr)$, at infinite dilution from water to aqueous THFA solution have been evaluated from ϕ_v° data , using the equation [27].

$\phi_v^\circ(tr) = \phi_v^\circ(in\ aqueous\ \text{THFA}) - \phi_v^\circ(\text{in water})$.....(6)

The values of $\phi_v^\circ\ (tr)$ are summarized in table 7. The values of ϕ_v° of Threonine in mixed liquids (THFA+water) are higher than those in aqueous solution, $\phi_v^\circ\ (tr)$ are positive for all solutions studied.

The $\phi_v^\circ\ (tr)$ values can be explained on the basis of co-sphere overlap model in terms of solute –co-solute interaction. According to this model , hydrophilic – ionic group interaction contribute positively.

Table(1): Molarity, Molality ,density,viscosity,apparent molal volume,Gibbs free energy of activation for viscous flow,relative viscosity and parameters of Jones-Dole coefficients in aqueous solution at 298.15K.

C ($mol.dm^{-3}$)	M ($mol.Kg^{-1}$)	ρ ($g.cm^{-3}$)	η (cp)	ϕ_v ($cm^3.mol^{-1}$)	ΔG* ($J.mol^{-1}$)	η_r	Jones-Dole B-coefficient
0.0000	0.0000	0.99071	0.89243	0.0000	0.0000		0.1725
0.1	0.10170	0.99516	0.91336	75.19752	60613	1.02345	
0.2	0.20492	0.99979	0.93701	74.29009	60700	1.04995	
0.3	0.30968	1.00444	0.96015	73.91998	60777	1.07588	
0.4	0.41602	1.00909	0.97678	73.73489	60834	1.09452	
0.5	0.52399	1.01371	0.99344	73.68409	60893	1.11318	
0.6	0.63359	1.01838	1.00350	73.56667	60954	1.12446	
0.7	0.74473	1.02323	1.01941	73.16992	60941	1.14229	
0.8	0.85753	1.02811	1.03573	72.92741	60958	1.16057	
0.9	0.97202	1.03301	1.05167	72.67562	60974	1.17843	
1.0	1.08808	1.03805	1.07894	72.33196	60987	1.20899	

Table(2): Molarity, Molality ,density,viscosity,apparent molal volume,Gibbs free energy of activation for viscous flow,relative viscosity and parameters of Jones-Dole coefficients in 2.5% aqueous solution of tetrahydrofurfuryl alcohol at 298.15K.

C ($mol.dm^{-3}$)	M ($mol.Kg^{-1}$)	ρ ($g.cm^{-3}$)	η (cp)	ϕ_v ($cm^3.mol^{-1}$)	ΔG^* ($J.mol^{-1}$)	η_r	Jones-Dole B-coefficient
0.0000	0.0000	0.99614	0.92492	0.0000	0.0000		0.19
0.1	0.10117	1.00033	0.96986	77.39809	65041	1.04859	
0.2	0.20389	1.00472	0.97224	76.39470	65050	1.05116	
0.3	0.30818	1.00915	0.99086	75.92602	65080	1.07129	
0.4	0.41409	1.01357	1.01226	75.71689	65127	1.09443	
0.5	0.52156	1.01816	1.03483	75.25008	65185	1.11883	
0.6	0.63039	1.02318	1.05241	74.21925	65208	1.13784	
0.7	0.74087	1.02813	1.07706	73.58350	65257	1.16449	
0.8	0.85270	1.03339	1.09844	72.71814	65297	1.18761	
0.9	0.96647	1.03832	1.11839	72.41240	65334	1.20917	
1.0	1.08205	1.04317	1.12398	72.24863	65339	1.21522	

Table(3): Molarity, Molality ,density,viscosity,apparent molal volume,Gibbs free energy of activation for viscous flow,relative viscosity and parameters of Jones-Dole coefficients in 5% aqueous solution of tetrahydrofurfuryl alcohol at 298.15K.

C ($mol.dm^{-3}$)	M ($mol.Kg^{-1}$)	ρ ($g.cm^{-3}$)	η (cp)	ϕ_v ($cm^3.mol^{-1}$)	ΔG^* ($J.mol^{-1}$)	η_r	Jones-Dole B-coefficient
0.0000	0.0000	1.00122	0.94740	0.0000	0.0000		0.2457
0.1	0.10067	1.00522	0.99466	78.90266	65092	1.04988	
0.2	0.20289	1.00956	1.03250	77.20593	65178	1.08982	
0.3	0.30668	1.01391	1.06899	76.64595	65257	1.12834	
0.4	0.41207	1.01832	1.09166	76.15746	65303	1.15227	
0.5	0.51897	1.02294	1.11268	75.46747	65343	1.17446	
0.6	0.62743	1.02768	1.13170	74.80847	65377	1.19453	
0.7	0.73727	1.03275	1.16186	73.86733	65434	1.22637	
0.8	0.84872	1.03779	1.18101	73.19793	65492	1.24658	
0.9	0.96194	1.04271	1.20165	72.81120	65502	1.26837	
1.0	1.07658	1.04787	1.23206	72.26215	65567	1.30046	

Table(4): Molarity, Molality ,density,viscosity,apparent molal volume,Gibbs free energy of activation for viscous flow,relative viscosity and parameters of Jones-Dole coefficients in 7.5% aqueous solution of tetrahydrofurfuryl alcohol at 298.15K.

C ($mol.dm^{-3}$)	M ($mol.Kg^{-1}$)	ρ ($g.cm^{-3}$)	η (cp)	ϕ_v ($cm^3.mol^{-1}$)	ΔG^* ($J.mol^{-1}$)	η_r	Jones-Dole B-coefficient
0.0000	0.0000	1.00616	0.98295	0.0000	0.0000		0.3197
0.1	0.10020	1.00995	1.02641	80.60533	65158	1.04421	
0.2	0.20198	1.01398	1.07386	79.41032	65264	1.09249	
0.3	0.30540	1.01802	1.10733	78.98016	65335	1.12654	
0.4	0.41042	1.02221	1.15119	78.39213	65425	1.17116	
0.5	0.51701	1.02660	1.18189	77.64184	65483	1.20239	
0.6	0.62534	1.03087	1.20009	77.33995	65551	1.22091	
0.7	0.73542	1.03514	1.23717	76.13138	65583	1.25863	
0.8	0.84696	1.03975	1.27406	75.38548	65648	1.29641	
0.9	0.96007	1.04453	1.30490	74.02152	65702	1.32753	
1.0	1.07455	1.04962	1.34829	73.44734	65771	1.37168	

Table(5): Molarity, Molality ,density, viscosity, apparent molal volume, Gibbs free energy of activation for viscous flow, relative viscosity and parameters of Jones-Dole coefficients in 10% aqueous solution of tetrahydrofurfuryl alcohol at 298.15K.

C ($mol.dm^{-3}$)	M ($mol.Kg^{-1}$)	ρ ($g.cm^{-3}$)	η (cp)	ϕ_v ($cm^3.mol^{-1}$)	ΔG* ($J.mol^{-1}$)	η_r	Jones-Dole B-coefficient
0.0000	0.0000	1.01093	1.02447	0.0000	0.0000		0.3543
0.1	0.09976	1.01432	1.12690	84.18013	65379	1.09998	
0.2	0.20121	1.01779	1.16680	83.78419	65461	1.13893	
0.3	0.30430	1.02157	1.18836	82.63011	65501	1.15998	
0.4	0.40912	1.02532	1.21846	82.12767	65558	1.18936	
0.5	0.51565	1.02915	1.25333	81.66732	65623	1.22339	
0.6	0.62382	1.03321	1.28298	80.98146	65675	1.25234	
0.7	0.73364	1.03744	1.35801	80.25137	65809	1.32557	
0.8	0.84433	1.04269	1.38797	78.44295	65855	1.35482	
0.9	0.95678	1.04775	1.43334	77.24421	65927	1.39918	
1.0	1.07065	1.05301	1.47829	76.08808	65995	1.44298	

Table(6): Limiting partial molal volume and the slop at 298.15K.

Conc.	$\phi_v°$	S_v
0%	74.980	-2.4528
2.5%	77.748	-5.4303
5%	78.9	-6.5351
7.5%	81.254	-7.128
10%	85.472	-8.217

Table (7): Partial molal volumes of transfer at infinite dilution $\phi_v°$ (tr) of Threonine from water to mixed liguid (THFA+water) at 298.15K.

Threonine in mixed liquid (water +THFA)	$\phi_v°$ (tr) ($cm^3.mol^{-1}$)
2.5% THFA	2.768
5% THFA	3.92
7.5% THFA	6.274
10% THFA	10.492

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تأثرات الحامض الاميني الثرونين في محلول تتراهيدروفورفورايل الكحول وفي المحلول المائي في درجة حرارة 298.15 كلفن

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الخلاصة

قيست كثافة ρ ولزوجة η محاليل مختلفة للحامض الاميني الثرونين في المحلول المائي وفي محلول تترا هيدروفورفورايل الكحول في درجة حرارة 298.15 كلفن . استخدمت النتائج لحساب الحجم المولاري الظاهري ϕ_v , الحجم المولاري الظاهري المحدد ϕ_v° , الميل S_v, حجم الانتقال $\phi_v^\circ(tr)$, طاقة جبس الحرة للانسياب اللزج للمحلول $\Delta G^*_{1,2}$ ومعامل جونس – دول–B.

تمت مناقشة طبيعة التآثر من نوع مذاب–مذيب ومذاب–مذاب من خلال قيمة ϕ_v° , S_v وقيمة معامل جونس – دول–B.

الكلمات المفتاحية: اللزوجة, الكثافة, الثرونين, تتراهيدروفورفورايل الكحول